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August 4, 2005

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2005 AUG 16 AM 10:00

Mr. Stephen L. Johnson
Administrator
U.S. Environmental Protection Agency
P.O. Box 1473
Merrifield, VA 22116

Re: Phosgene Panel HPV Chemical Challenge Program: Response to EPA Comments
Regarding Phosgene (CAS Number 75-44-5)

Dear Administrator Johnson:

This document is being submitted on behalf of the American Chemistry Council's Phosgene Panel (Panel) which wishes to provide an update to EPA on changes to the names of the companies sponsoring phosgene and the name of the Panel Manager contact, and to respond to EPA comments on the HPV Test Plan and Robust Summaries. The sponsoring Panel members are: BASF Corporation; Bayer MaterialScience, LLC (formerly Bayer Corporation); The Dow Chemical Company; DuPont; GE Advanced Materials (formerly GE Plastics Company); Lyondell Chemical Company; PPG Industries, Inc.; Rubicon LLC; Syngenta Inc. (formerly Syngenta Crop Protection and more formerly Zeneca Ag Products); and, ISOCHEM Groupe SNPE (formerly VanDeMark, Inc.).

This submission also is being sent electronically to the following e-mail addresses:

Oppt.ncic@epa.gov
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In the process of reviewing the Panel's submission to EPA for the HPV Challenge Program against the EPA contractor's work product for the pilot HPV Information System (HPVIS) for phosgene, it was discovered that a Panel response to EPA's comment regarding fugacity had never been submitted. The Panel would like to take this opportunity to respond at this time and request that this information be incorporated into the HPVIS database.

The Panel would like to thank the Agency for its constructive review and comments on the HPV Test Plan and Robust Summaries for phosgene which were received on November 18, 2003. In light of the hazardous properties and unique reactivity of this chemical, we acknowledge the Agency's request for additional information to address the SIDS endpoint of "Transport Between Environmental Compartments (Fugacity)." Our rationale for addressing this critical endpoint is given below, and a corresponding Robust Summary for the "Transport Between Environmental Compartments (Fugacity)" endpoint is included in the attached document (pdf file).

EPA Comment:

The submitter needs to clarify in the fugacity robust summary the assertion that the diffusion coefficient is the key parameter for determining transport of phosgene from the atmosphere to condensed aqueous phases.



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EPA Comment:

Fugacity. No fugacity data were provided by the submitter for phosgene. The submitter stated that "due to the instantaneous reaction of phosgene in water, the transport of the material between environmental compartments can not be predicted using equilibrium distribution coefficients involving the water phase." The submitter further stated that "the liquid-phase diffusion coefficient, as reported by Manogue and Pigford (1960) is a key parameter for determining transport of phosgene from the atmosphere to condensed aqueous phases." However, EPA believes that the aqueous-phase diffusion coefficient does not describe the transport of phosgene from the air to the condensed aqueous phase, but describes the diffusion of phosgene within the aqueous phase. The submitter should clarify in a technical discussion the assertion that the liquid-phase diffusion coefficient is the key parameter for determining transport of phosgene from the atmosphere to condensed aqueous phases.

Response:

The Level III fugacity model described by Mackay¹ is OECD's recommended method for determining the transport of a chemical between environmental compartments of air, water, soil, and sediments, when the modes and magnitudes of emission to these media are known.² The Level III model allows a prediction of the environmental fate and distribution of a chemical resulting from a combination of reactive, advective, and inter-media transport processes. The required inputs for the Level III fugacity model include molecular weight, melting point, vapor pressure, water solubility, log octanol-water partition coefficient ($\log K_{ow}$), and the temperature of the environment to be simulated (typically 20 or 25° C). The half-lives for relevant destructive chemical reactions in these various media are also required inputs of the model. Of these required inputs for the Level III model, the molecular weight, melting point, and vapor pressure of phosgene have been measured using accepted experimental procedures. However, due to the reactivity of phosgene in water, accurately measured values of water solubility and $\log K_{ow}$ are lacking. Because values for these input parameters cannot be reliably determined, it was initially concluded that the Level III model could not be applied to addressing the "Transport Between Environmental Compartments" endpoint for phosgene. However, there are currently no alternate multimedia environmental fate/transport models available which have applicability to highly reactive chemicals, and acceptability equal to that of the Level III fugacity model. Therefore, a sensitivity analysis was performed to examine the impact of water solubility and $\log K_{ow}$ values on the Level III model output for phosgene. This analysis, summarized in Table 1, showed that input water solubility and K_{ow} values can be varied by over four orders of magnitude with virtually no impact on the predicted environmental distribution or total environmental residence time for phosgene. It was therefore concluded that the fate and lifetime of phosgene are largely dictated by reactive and advective processes occurring exclusively within the atmosphere, and that fate and transport in soil, water, and sediments are of much less significance. The Level III fugacity model incorporates accepted values for the dimensions, densities, advective flow residence times, and deposition processes occurring in the atmosphere. Therefore, with careful consideration of the input parameters for phosgene, the Level III fugacity model was used to address the "Transport Between Environmental Compartments" endpoint.

¹ Mackay, D., Di Guardao, A., Patterson, S., and C. E. Cowan. 1996. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. *Environ. Toxicol. Chem.* 15(9):1627-1637.

² OECD. 20002. Manual for Investigation of HPV Chemicals, Chapter 2: SIDS, The SIDS Plan and the SIDS Dossier. Annex 1: Guidance for Completing a SIDS Dossier. Pp. 41-42. Available at: <http://www.oecd.org/dataoecd/60/44/1947485.pdf>.

Table 1. Summary of Level III model outputs for phosgene using a wide range of input water solubility and log K_{ow}

Input Parameters*	Percentage and amount distributed to				Residence Time (hrs.)
	Air	Water	Soil	Sediment	
Water sol. = 1 g/m ³ log K_{ow} = -1.0	100.0 % 2000 kg	4.9×10^{-6} % 9.9×10^{-5} kg	9.6×10^{-4} % 1.9×10^{-2} kg	2.0×10^{-9} % 4.0×10^{-8} kg	2.0
Water sol. = 1 g/m ³ log K_{ow} = 3.0	100.0 % 2000 kg	4.9×10^{-6} % 9.9×10^{-5} kg	9.6×10^{-4} % 1.9×10^{-2} kg	3.9×10^{-8} % 7.7×10^{-7} kg	2.0
Water sol. = 10,000 g/m ³ log K_{ow} = -1.0	100.0 % 2000 kg	4.8×10^{-2} % 1.0 kg	3.4×10^{-3} % 6.8×10^{-2} kg	1.9×10^{-5} % 3.9×10^{-4} kg	2.0
Water sol. = 10,000 g/m ³ log K_{ow} = 3.0	99.9 % 2000 kg	4.8×10^{-2} % 1.0 kg	8.0×10^{-2} % 1.6 kg	3.8×10^{-4} % 7.6×10^{-3} kg	2.0
Water sol. = 100 g/m ³ log K_{ow} = 2.0	100.0 % 2000 kg	4.8×10^{-4} % 9.7×10^{-3} kg	1.0×10^{-3} % 2.1×10^{-2} kg	4.2×10^{-7} % 8.3×10^{-6} kg	2.0
**Water sol. = 8,940 g/m ³ log K_{ow} = -0.71	100.0 % 2000 kg	4.8×10^{-2} % 1.0 kg	3.4×10^{-3} % 6.8×10^{-2} kg	1.9×10^{-5} % 3.9×10^{-4} kg	2.0

*all model simulations used molecular wt. = 98.92, vapor press. = 161,600 Pa, melt point = -128° C, data temp. of 20° C, 1000 kg/hr. emissions to air, and no reactivity in air or water.

**simulation presented in Robust Summary, using experimentally estimated water solubility⁵ and predicted log K_{ow} .⁹

In the initial submission of the HPV Test Plan and Robust Summaries for phosgene, it was stated that the aqueous-phase diffusion coefficient is a key parameter for determining the transport of this chemical from the atmosphere to condensed aqueous phases. This transfer of a chemical between contiguous air and water phases can occur by two types of processes, both of which are simulated by the Level III fugacity model. The first type of transfer process involves a bulk material transfer, where a volume of one phase physically moves into or through another phase, thus carrying the chemical with it. The second type of transfer involves molecular diffusion processes, which are driven by fugacity differences among the two interfacing phases. This diffusive transfer process is described by Mackay in terms of a "two resistance" model,³ where Fick's Law of diffusion is applied to each of the two adjacent phases in series. Just as the flow of electrical current is controlled by only the larger of two resistances connected in series, the diffusive flow of a chemical between two phases is controlled by the largest "diffusive resistance" among these contiguous phases. The diffusion of a chemical proceeds from the phase having higher fugacity to the phase having lower fugacity, and the overall rate of transfer is regulated by the phase where diffusion is slowest, or "diffusive resistance" is highest. Together with estimated volumes and interfacial surface areas for air and water phases of the default Level III environment, these diffusivities are used to derive mass transfer coefficients (in moles/hr.) for diffusive transport occurring on both sides of the air/water interface. In the Level III fugacity model, default mass transfer coefficients of 5 mole/hr. for air side air-water transfer, and 0.5 m/hr. for water side air-water transfer are derived, based on default diffusivities of 0.11 cm²/sec. in air, and 1.1×10^{-5} cm²/sec. in water, respectively.⁴ The default diffusivities used by the Level III model are in close agreement with diffusion coefficients reported for phosgene in water (1.27×10^{-5} cm²/sec. at 25° C)⁵ and in air (0.095 cm²/sec. at 0° C).⁶ The diffusion of phosgene into and

³ Mackay, D. and S. Paterson. 1982. Fugacity revisited: The fugacity approach to environmental transport. *Environ. Sci. Technol.* 16(12):654A-660A.

⁴ Mackay, D., Patterson, S., Cheung, B., and W. B. Neely. 1985. Evaluating the environmental behavior of chemicals with a Level III fugacity model. *Chemosphere* 14(3/4):335-374.

⁵ Manogue, W. H. and R. L. Pigford. 1960. The kinetics of the absorption of phosgene into water and aqueous solutions. *A. I. Ch. E. Journal* 6(3):494-500.

⁶ Klotz, I. M. and D. K. Miller. 1947. Diffusion coefficients and molecular radii of hydrogen cyanide, cyanogen chloride, phosgene, and chloropicrin. *J. Am. Chem. Soc.* 69:2557-2558.

through water is slower than that into and through air, and has been shown to be the rate-limiting step in aqueous-phase hydrolysis of the material.⁵ Hydrolysis of phosgene in the aqueous phase limits the amount of material which can diffuse back into the air phase. Therefore, the aqueous-phase diffusion of phosgene is considered a key parameter which influences mass transfer of phosgene from air to water.

Modified Robust Summary for "Transport Between Environmental Compartments"

On the basis of the above technical discussion, a Robust Summary was created for the "Transport Between Environmental Compartments" endpoint, which includes a summary of output from the Level III fugacity model. The input parameters for the Level III model, along with their justification, are noted below.

Simulated Emission Scenario:

It is concluded that industrial emissions of phosgene to the environment would be expected to occur as vapor-phase emissions into the atmosphere. However, these emissions would likely be a very small fraction of the total sources of tropospheric phosgene. Helas and Wilson⁷ estimate that photo-oxidation of chlorinated hydrocarbons (of both natural and anthropogenic origins) results in a tropospheric phosgene production rate of $>2 \times 10^9$ lb/yr. Emissions via water discharges are not practical, due to the rapid reaction and short half-life (0.026 sec.) of the material in aqueous media.⁵ Since phosgene is anticipated to be used as an on-site, captive intermediate, there is little potential for direct spillage of the material to soil or water from transportation accidents. These assumptions are supported by the total U.S. phosgene emissions reported for year 2001 of 16,383 lbs., of which 98.5% were reported as on-site emissions to the atmosphere.⁸ While these reported emissions are equivalent to only 0.9 kg/hr. spread over one year, the recommended default emission rate for the Level III model of 1,000 kg/hr. was used.

Reaction Half-lives:

Atmospheric degradation processes such as direct photolysis, and indirect photolytic reaction with ozone and hydroxyl radical, have been shown to be negligible for phosgene. The dominant process for removal of phosgene in the troposphere is expected to be hydrolytic reaction with water droplets in fog and clouds. Helas and Wilson estimated half-lives for this removal process over several different latitudes, and concluded that tropospheric half-lives will average approximately 10 hrs., and typically not exceed 24 hrs.⁷ Therefore, a half-life of 24 hrs. was used as the Level III input for reaction in air. The reported half-life for hydrolysis of phosgene in water is 0.026 sec., and this half-life was used as the Level III model input for reaction in water.⁵ Compared to air and water, phosgene is expected to have negligible contact with other environmental media such as soil, sediment, and fish. Therefore, the reactivities of phosgene in these media were entered into the Level III model as negligible (1.0×10^{11} hr.).

Physical/Chemical Properties:

The physical/chemical properties input into the Level III model for phosgene included a molecular weight of 98.92 g/mole, melting point of -128° C, and vapor pressure of 161,600 Pascal (at 20° C), as previously presented in the Robust Summaries for these endpoints. A water solubility of 8,940 g/m³ at 20° C was derived from the data reported by Manogue and Pigford,⁵

⁷ Helas, G. and S. R. Wilson. 1992. On sources and sinks of phosgene in the troposphere. *Atmospheric Environment* 26A(16):2975-2982.

⁸ U.S. EPA. 2004. Toxics Release Inventory (TRI) Database for year 2001. United States Environmental Protection Agency, Washington, D. C. Available at: <http://www.epa.gov/tri/>

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while a log K_{ow} of -0.71 is estimated from the structure of phosgene.⁹ While these latter two properties cannot be reliably measured, Level III model was shown to be insensitive to water solubility over a range of 1 to 10,000 g/m³ and log K_{ow} over a range of -1.0 to 3.0 when the other input properties of phosgene were held constant. Input of these water solubility and log K_{ow} was for illustrative purposes, to allow output calculations to be performed by the Level III model.

We are confident that we have fully addressed the Agency's comments regarding the environmental fate and distribution of phosgene, using the Level III fugacity model. The Panel wishes to thank the Agency for its comments, which have resulted in an improved HPV submission for this important chemical intermediate.

If you have any questions regarding this submittal, please contact Elizabeth Festa Watson, Manager of the Phosgene Panel, at 703/741-5629 or via e-mail at elizabeth_watson@americanchemistry.com. Please note that Ms. Watson has replaced Dr. Anne LeHuray as the Panel contact.

Sincerely yours,

Courtney M. Price
Vice President, CHEMSTAR

Attachment

Cc: Phosgene Panel
Christina Franz/ACC
Jim Keith/ACC
Oscar Hernandez/EPA OPPT
Brion Cook/EPA OPPT

⁹ U.S. EPA. 2000. WSKOWWIN software, version v1.40. United States Environmental Protection Agency, Office of Pollution Prevention and Toxics, Washington, D. C. Available at: <http://www.epa.gov/oppt/exposure/docs/episuitd1.htm>.

Attachment
Modified Robust Summary for "Transport Between Environmental Compartments"
 August 2005

TEST SUBSTANCE

Identity: Phosgene (CAS No. 75-44-5)

Remarks:

METHOD

Test: Predicted transport between environmental compartments

Method: Level III Fugacity Model

Year: 2002

Remarks: Level III model version 2.70 (2002). Obtained from the Canadian Environmental Modeling Centre, Trent University, Peterborough, Ontario, Canada.

Input Parameters for Level III Modeling of Phosgene:

Property	Value	Source
Data Temperature (°C)	20	Default environmental temperature
Chemical Type	1	Type 1 indicates chemical can partition into all environmental compartments
Molecular Mass (g/mol)	98.92	Calculated from molecular structure
Water Solubility (g/m ³)	8,940	Experimentally estimated value at 20° C [1]
Vapor Pressure @ 20° C (Pa)	161,600	Recommended measured value [1]
Melting Point (°C)	-127.8	Recommended measured value [1]
Estimated Henry's Law Constant (Pa m ³ /mol)	1,788	Calculated from vapor pressure and water solubility
Log Octanol-Water Partition Coefficient (log K _{ow})	-0.71	Predicted value based on structure fragments [2]
Reaction Half-lives (hr.) Input to Level III Model		
Air (vapor phase)	24	Estimated half-life for hydrolysis in fog, clouds [3]
Water (no susp. solids)	2.1 x 10 ⁻⁵	Based on measured hydrolysis half-life at 20° C [4]
Soil	*1.0 x 10 ¹¹	Material has negligible contact with soil
Sediment	*1.0 x 10 ¹¹	Contact with sediment, suspended sediment, and fish is not expected, due to rapid hydrolysis
Suspended Sediment	*1.0 x 10 ¹¹	
Fish	*1.0 x 10 ¹¹	
Aerosol	*1.0 x 10 ¹¹	Aerosol emissions not expected
Simulated emissions	0.9 kg/hr to air 1,000 kg/hr to air	Based on year 2001 reported TRI emissions [5] Level III recommended default emission rate
Simulated environment	-	Default Level III Environment [6]

* Default value used in Level III model when reactivity is expected to be negligible in this compartment

RESULTS

Predicted environmental distribution and persistence of phosgene under reactive and non-reactive conditions

Emission Scenario	Percentage and amount distributed to				Residence Time (hrs.)
	Air	Water	Soil	Sediment	
1,000 kg/hr to air (advection and diffusion only)	100.0 % 2000 kg	4.8 x 10 ⁻² % 1.0 kg	3.4 x 10 ⁻³ % 6.8 x 10 ⁻² kg	1.9 x 10 ⁻⁵ % 3.9 x 10 ⁻⁴ kg	2.0
1,000 kg/hr to air (advection, diffusion, and reaction)	100.0 % 1,891 kg	4.5 x 10 ⁻³ % 8.6 x 10 ⁻⁸ kg	3.1 x 10 ⁻³ % 5.9 x 10 ⁻² kg	1.8 x 10 ⁻¹² % 3.4 x 10 ⁻¹¹ kg	1.89
0.9 kg/hr to air (advection, diffusion, and reaction)	100.0 % 1.7 kg	4.5 x 10 ⁻⁹ % 7.7 x 10 ⁻¹¹ kg	3.1 x 10 ⁻³ % 5.3 x 10 ⁻⁵ kg	1.8 x 10 ⁻¹² % 3.1 x 10 ⁻¹⁴ kg	1.89

CONCLUSIONS

Remarks: Phosgene is rapidly hydrolyzed in water, which prevents accurate measurements of water solubility and log K_{ow}. However, iterative sensitivity analyses showed that the Level III model output for phosgene is not affected by input water solubilities ranging from 1 to 10,000 g/m³, and input log K_{ow} ranging from -1.0 to 3.0. Values for these properties, estimated

from experimental data (water sol.) and structure-activity relationships ($\log K_{ow}$), were required inputs to allow calculations by the Level III model. Each of the simulated emission scenarios supports the conclusion that phosgene will reside exclusively in the atmosphere upon its emission to the environment. Model simulations were conducted with and without reaction of phosgene in air and water to demonstrate the dominant influence of atmospheric advection and diffusion process on the environmental persistence of phosgene. The Level III model indicates rapid dissipation of phosgene in the atmosphere, with a predicted atmospheric residence time of approximately 2 hrs.

DATA QUALITY

Reliability: 2(f)

Remarks: Accepted calculation method

REFERENCES

1. International Programme on Chemical Safety (IPCS). 1995. Environmental Health Criteria for Phosgene, Second Draft. United Nations Environment Programme, World Health Organization, PCS/EHC.95.47, October 1995.
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3. Helas, G. and S. R. Wilson. 1992. On sources and sinks of phosgene in the troposphere. *Atmospheric Environment* 26A(16):2975-2982.
4. Manogue, W. H. and R. L. Pigford. 1960. The kinetics of the absorption of phosgene into water and aqueous solutions. *A. I. Ch. E. Journal*. 6(3):494-500.
5. U.S. EPA. 2004. Toxics Release Inventory (TRI) Database for year 2001. United States Environmental Protection Agency, Washington, D. C. Available at: <http://www.epa.gov/tri/>
6. Mackay, D., 2001. Multimedia Environmental Models: The Fugacity Approach. Lewis Publishers, CRC Press, Boca Raton, FL. Models available at: <http://www.trentu.ca/cemc/models.html>

FLAG

Critical study for SIDS endpoint